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FINAL REPORT

ACTIVITIES IN THE OFF GAS FROM THE METAL SOLUTION STEP

PROBLEM ASSIGNMENT NO. 242-X8P

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Table of Contents

ABSTRACT

Active xenon and iodine have been measured in the
direct off-gas from the 205 Building metal dis-
solver. Xenon is given off only during actual dis-
solving of metal and shows average intensities
slightly less than 10^{-8} curies/cc over such time
intervals with marked intensity peaks at the be-
ginning of the solution reaction. Iodine is given
off rather continuously and averages between
1×10^{-10} to 2×10^{-10} curies/cc. These concentra-
tions are reduced by a factor of about 500 by the
ventilating air before the gases are discharged
from the stack.

Material balances show that essentially all of the
xenon but only 2 to 5% of the iodine present in the
metal at the time of solution are discharged through
the stack. Data covering a period of continuous
monitoring are given and suggestions for obtaining
continuous intensity records are made.

I. Introduction

The dissolving of uranium metal, which is the first step in the chemical separation process, releases volatile fission products. These join the nitrogen oxide products of the solution reaction and are discharged into the atmosphere by the 200 area stack. Xe^{133} (5.3 days) and I^{131} (8 days) are the main active elements in the dissolver off-gas because short lived products decay to negligible activities during the hold-up interval. The Xe or I are a potential health hazard in the vicinity of the plant. This report describes the experimental work which determined the quantities of these elements discharged by the stack and their time distribution. The experiments also suggest procedures for putting these measurements on a continually recording basis for legal purposes.

Ruthenium is volatile in the oxidized state and also represents a potential hazard. None of our measurements of the activity in the off-gas have indicated its presence but no specific attempts to find it have been made. However, it is known to be given off to some extent from cell 2.

The actual amount of Xe and I present in a one-third ton metal charge may be estimated by the following factors under the assumptions that these activities have reached equilibrium in the pile and that the metal comes from a region of average neutron flux:

3.1×10^{16} fissions/1000 kw/sec.
3.7×10^{10} conversion to curies
$.01$ fraction pile metal in charge
$.052$ branching ratio for Xe
$.023$ branching ratio for I.

Since at equilibrium the amount of a fission product in the pile equals the product of its branching ratio times the number of fissions, the total 5.3 d. xenon activity in the pile is

$$\frac{3.1 \times 10^{16} \times .052}{3.7 \times 10^{10}} = 4.35 \times 10^4 \text{ curies,}$$

and the total 8.0 d. iodine activity is

$$\frac{3.1 \times 10^{16} \times .023}{3.7 \times 10^{10}} = 1.92 \times 10^4 \text{ curies.}$$

If the hold-up time for a third-ton charge of metal is 32 days the xenon will have decayed through approximately 6 half-lives and the metal will contain $4.35 \times 10^4 \times .01 \times 1/2^6$ or 6.8 curies and similarly, the iodine having decayed through 4 half-lives, the metal will contain 12 curies of iodine.

Material balances based on the above calculations show approximately 100% xenon and 2 to 5% iodine is discharged from the dissolver to the stack.

Almost all of the experimental work has been done by sampling the gas in the off-gas line before dilution with the 205 Building ventilating air in the stack. Since the flow in the off-gas line is approximately 100 cfm and the ventilating air 40,000 to 50,000 cfm a dilution of 400 to 500 occurs in the stack. A similar value has been obtained by comparing the xenon intensity in the off-gas line and in the stack through the sampling tube 50 ft. from the ground. No iodine measurements from the 50 ft. stack samples have been made because of the much lower concentration.

II. Apparatus

The off-gas from the 205 dissolver pass through a 4" stainless steel pipe into the stack. A small line tapped from this 4" line leads to Building 204 where samples of the gas may be drawn from this line through the monitoring apparatus by means of a steam aspirator which discharges back into the stack via the 4" line and maintains the monitoring system below atmospheric pressure.

The monitoring apparatus at present consists of:

(a) an orifice, the pressure differential across which is recorded by a Ring Balance flow meter to give a record of the volume of gas through the apparatus;

(b) 2 500 ml water scrubbers with glass beads;

(c) drying apparatus, consisting of a water-cooled spiral condenser, a drying bottle filled with glass wool, and two bottles filled with anhydrous $CaCl_2$ lumps;

(d) an ion chamber, with Beckman amplifier and Leeds and Northrup Micromax.

Valves on the intake and vacuum lines make it possible to regulate the flow and to trap samples of the gas in the apparatus. A valved air-bleed

on the intake side is used to purge the system. All surfaces exposed
to the acid fumes are of either stainless steel, glass, duPont 6-x
(PTFE), or saran. Saran tubing was used in connecting the scrubbing
and drying apparatus in order to make the experimental set-up more
flexible.

In the latest procedure the iodine component of the activity
of the off-gas is separated by scrubbing the gas through water and then
measuring the activity retained in the wash water with a calibrated
electroscope.

The xenon component is measured by passing the scrubbed and
dried gas through a stainless steel ion chamber (Figure 1). The re-
sultant current is amplified by a Beckman micromicroammeter and re-
corded by a Leeds and Northrup Micromax.

The ionization current observed in the ion chamber arises
primarily from Xe beta disintegrations occurring in the gas in the
chamber. In order that the reading should be independent of the
residual ionization in the gas when entering the chamber (and conse-
quently independent of the gas flow rate) this residual ionization is
conducted to ground in the central tube of the chamber. The high
voltage insulator is a complete ring and makes the gas enter the
chamber through this central tube. In order to protect the main in-
sulator from the gases it was placed at the top of the neck of the
chamber, protected with a baffle, and provision was made for the
vacuum of the system to draw in dry air above the baffle. Since it
was later found necessary to dry the total gas entering the chamber
in order to prevent the collected liquids from shorting out the screw
heads in the saran ring insulator to ground, it was found possible to
dispense with the dry air bleed.

This ion chamber was calibrated by passing a sample of the pile
cooling air through it and the pile air monitoring apparatus at the same
time. The pile cooling air contains active argon and the monitoring
chambers have been directly calibrated for the argon radiation (CP-1300).
The sensitivity of the stainless steel chamber for argon beta rays is
43 curies/cc/amp. A correction for the different specific ionization
of the low energy Xe beta rays (based on the assumption of a triangular
shape for the beta ray spectrum) indicates that the chamber is about
twice as sensitive for the Xe radiation as it is for the argon radiation.
This step, considered to be the least accurate part of the calibration,
results in a sensitivity of 20 curies/cc/amp.

III. Preliminary Experiments.

When the attempt was first made to pass the off-gas directly
into the ion chamber without preliminary scrubbing or drying, it was

Figure 1

Stainless Steel Ion Chamber
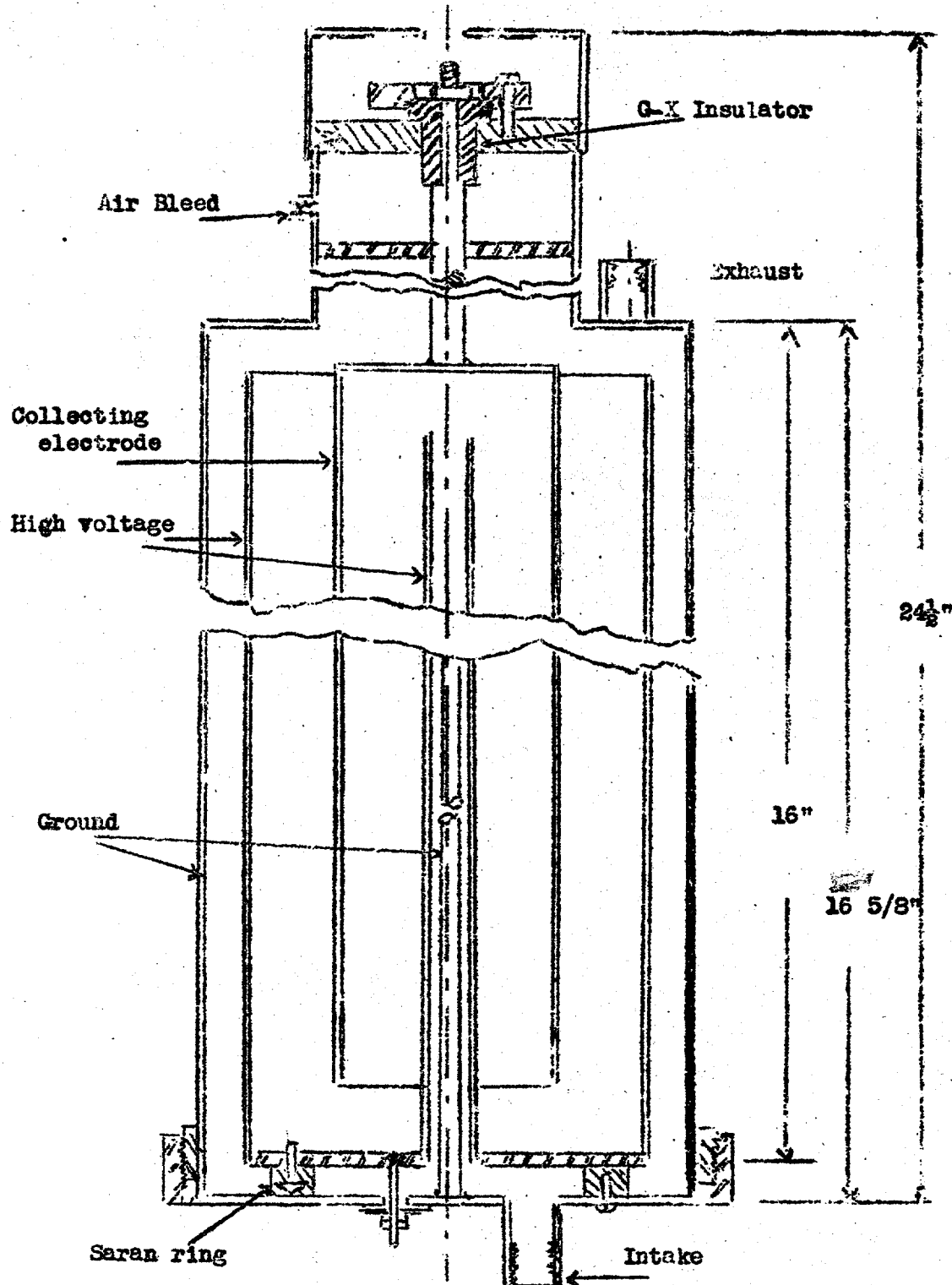
found that the water in the gas shorted out the chamber. Also an activity was deposited on the walls of the chamber which was found to decay with the half-life of 8.0 d. iodine. (An active deposit was also detected with an electroscope along the 4" line.)

Over a period of time, many tests were made to determine the most effective way of removing the iodine before it reached the chamber. The gas was passed through a bottle containing NaOH pellets. (This method proved effective in removing the iodine. However, the NaOH dissolved in the large amount of water in the gas, and the solution choked the trap. The heat of solution and neutralization (with the acid fumes) melted the saran connections. The iodine concentration was measured by extracting a part of the radioactive iodine with iodide carrier and counting the emitted beta particles with a Geiger-Mueller counter. The NaOH was dissolved in 1000 ml H_2O, a portion was neutralized with HNO_3, and I^- carrier was added. This was then reduced with $NaHSO_3$ and dissolved in the water layer. The I^- was precipitated from the water solution with Ag^+. With suitable corrections for self-absorption and for the loss due to the counter's geometry, the number of disintegrations per second in the original solution could be calculated and the iodine activity determined. A decay curve of the activity in the NaOH filter, showed only the 8 day iodine present.

Because the water in the off-gases caused traps filled with solid materials to become clogged, it was decided to try liquid traps. In order to obviate the tediousness of making an iodine extraction of each scrubbing solution used, an electroscope was calibrated to measure the curies per cc of a solution. This was done by placing 50 cc of solutions containing various activities of iodine in a "standard position" relative to the electroscope and noting the rate of deflection of the quartz fiber. Then by the procedure outlined above the iodine was extracted and the number of curies per cc of the original solution computed. The average value of the calibration from 7 different solutions is

$$1 \text{ div/min} = 5.6 \times 10^{-8} \text{ curies/cc.}$$

Further work with improved methods is being done on iodine analysis by the Analytical Division. The electroscope will be recalibrated with scrubbing solutions in which the iodine activity has been more accurately determined by this group. As soon as the figures are available the corrected calibration will be published. However, a single preliminary check indicated that the present calibration is essentially correct.*

*See Page 19 footnote.

The two gas scrubbers used as iodine traps are connected in series. During a course of experiments to test the relative ability of various solutions to retain iodine, water was placed in the first one and the solution to be tested in the second. It was expected that any large amount of iodine existing in the off-gas in a chemical form not readily taken up in the water would have been collected in the second trap.

Although various solutions were tried in the second scrubber, none appeared to be more effective than water. In the event that iodine in the form of HI were passing through the acid-saturated traps, .1 N $AgNO_3$ and .1 N $Hg(NO_3)_2$ solutions were tried, but the ratios of the activities in the first bottle filled with water to those of the second were not different from what one would have expected with two water scrubbers. When oxidizing solutions such as .1 f $Na_2Cr_2O_7$ and .1 f $KMnO_4$ were put in the scrubbers, it was found that the solutions soon were reduced by the nitrogen oxides in the gas and the results were vitiated.

The accompanying curves (Figure 2 and Figure 3) show the relation of the activity in the two scrubbers to the volume of gas passed through them. As the total volume of the gas through the monitoring apparatus increases the acid concentration in the scrubbers increases and they become less effective in retaining the iodine. When small volumes ($\sim$ 5 cu. ft.) are passed through H_2O traps, (i.e., when the acid concentration is small), practically all the iodine is retained in the first bottle, but with much larger volumes the activity in the second bottle rises until it becomes about half that of the first. Because of the impedence in the drying bottles and the fluctuations in the dissolver pressure, it is difficult to obtain a continuous gas flow through 3 water scrubbers in series. However, on two tests with three scrubbers the activity found in the third bottle was only 1% of the sum of the activities in the first two bottles after a volume of 31.3 cu.ft. had passed through the system, and 18% after a total gas volume of 125 cu.ft. had passed through.

In order to follow the distribution of the iodine activity with time it was decided to use two 500 ml scrubbing bottles, each filled with 350 cc of water and one pound of 3 to 5 mm glass beads. With gas flowing through the monitoring apparatus at a rate of about .1 cfm and the scrubbing water changed every 2 to 4 hours the traps are more than 95% efficient.

A test of the solutions for xenon in the water trap gave a negative result. During a xenon concentration peak the sampling line was closed and the traps and ion chamber purged with clean air. The ion chamber reading quickly dropped to background, indicating that no
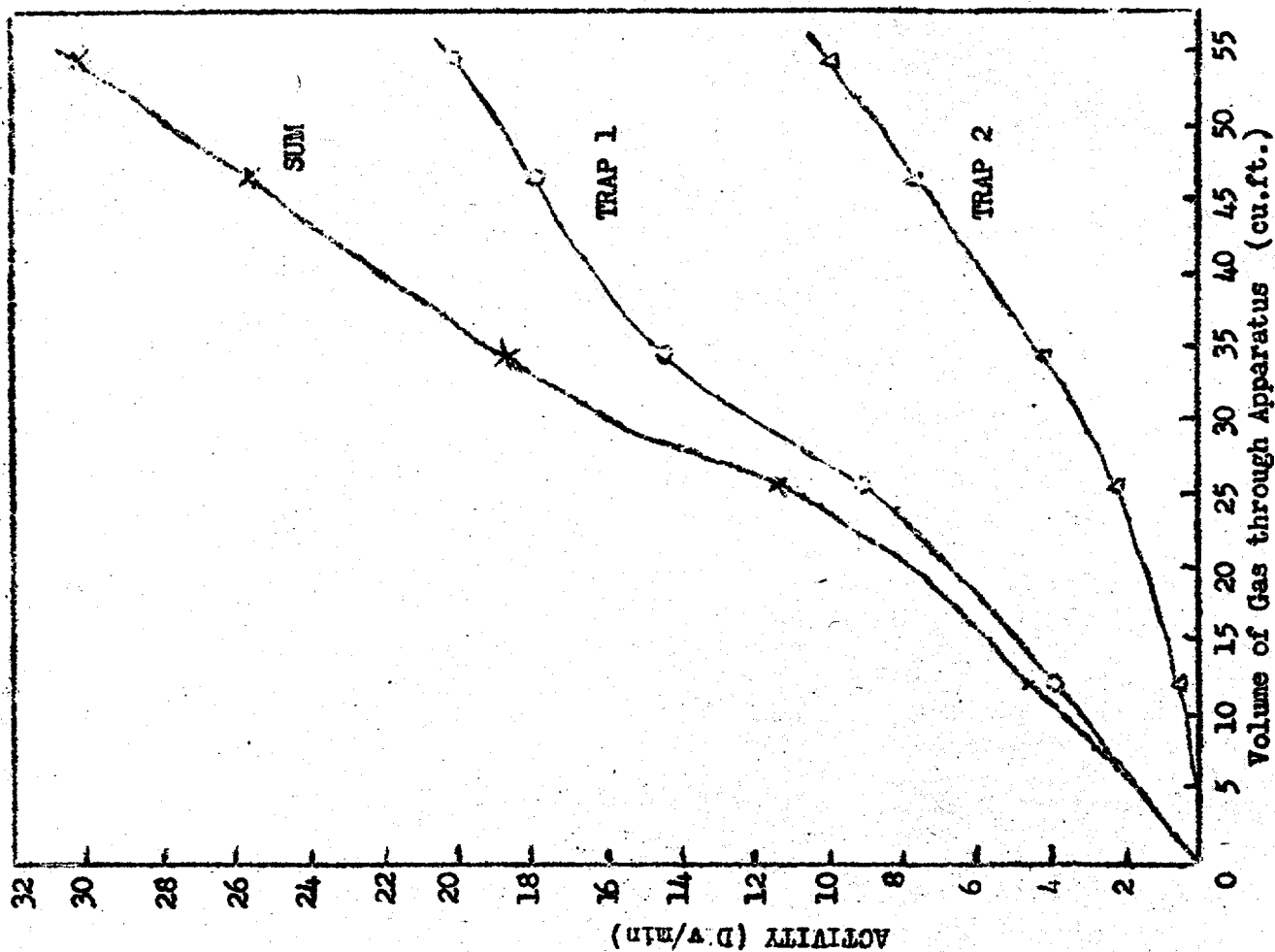
RISE OF IODINE ACTIVITY IN TRAPS
(Both Scrubbers Containing Glass Beads & 350 cc H$_2$O)

Figure 3
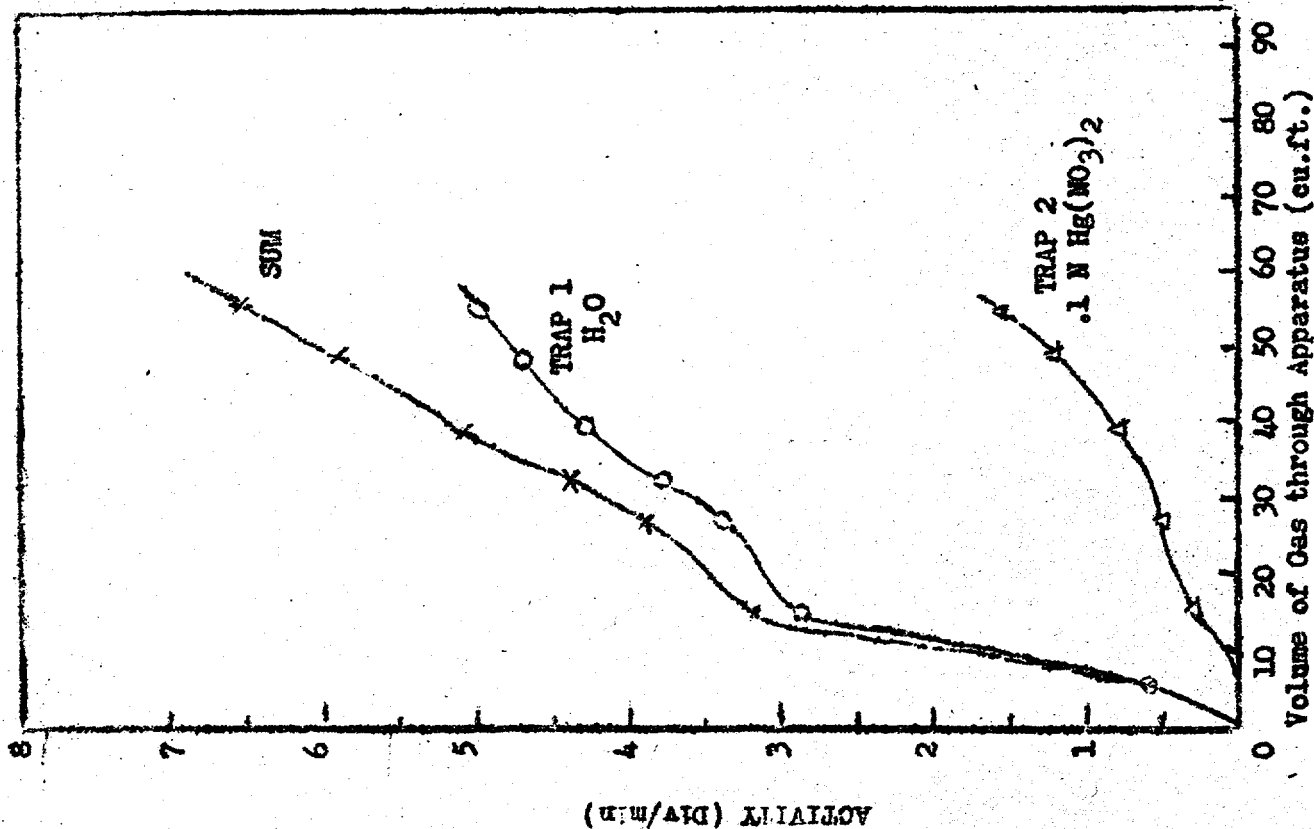
RISE OF IODINE ACTIVITY IN TRAPS
(1st Scrubber H$_2$O, 2nd Scrubber .1 N Hg(NO$_3$)$_2$ Sol.)

Figure 2

appreciable quantity of xenon came out the water traps. These traps have consistently shown only the eight day half-life of iodine when followed with an electroscope.

IV. Distribution of Xenon and Iodine Activities in Time

The activity of the Xe and I was followed continuously for the complete cycle of three dissolvings from April 19th to April 22nd and again from May 8th to May 11th. The accompanying graphs (Figure 4 and Figure 5) show the concentrations of Xe and I plotted against time. The smooth unbroken curve shows the relatively sharp peaks of Xe activity, which coincide closely with the actual times at which the dissolver is maintained at reacting temperature. The dotted line connects the points found for the iodine activity. Each point is plotted at the center of the period of time during which the volume of gas was passed through the collecting traps. The curies of iodine in both traps were added and the sum divided by the volume of gas passed through to obtain the concentration plotted.

It should be noted that only a few points were taken near the ends of the runs and hence these points represent long interval averages.

It can be seen that the iodine peaks trail the Xe peak intensities. Whether the iodine condenses along the lines and is gradually carried forward or whether it is slowly evolved in the long digestion process, as the curves for runs 97 and 115 seem to indicate, is not known. The iodine intensity may drop to zero between runs. A closer observation of the variation of activity with time would be necessary to determine this.

For a cycle of three dissolvings, enough metal (1 ton) for the cycle is placed in the dissolver in the beginning and an amount of acid is added sufficient to dissolve one third of the metal. Two similar dissolvings complete the cycle. The metal for Runs 95, 96 and 97 on April 19-22 was delivered in buckets 41, 24, and 49. Bucket 41 contained 195 slugs charged 12/7/43 and discharged 3/18/44; and 59 slugs charged 2/18/44 and discharged 3/18/44. The calculated amount of product for these 254 slugs was .787 g. Bucket 24 contained 267 slugs charged 2/18/44 and discharged 2/28/44, with a calculated product amount of .088 g. Bucket 49 contained 260 slugs charged 12/18/43 and discharged 3/16/44, with a calculated product amount of .963 g. The average cooling-off period, weighted with respect to the predicted product concentration was 35 days.

From the three dissolvings Run 95 assayed .639 g. of product, Run 96 .544 g., and Run 97 .525 g. to give a total of 1.71 g. as compared with the calculated 1.83 g.

DISTRIBUTION OF XENON AND IODINE ACTIVITIES WITH TIME
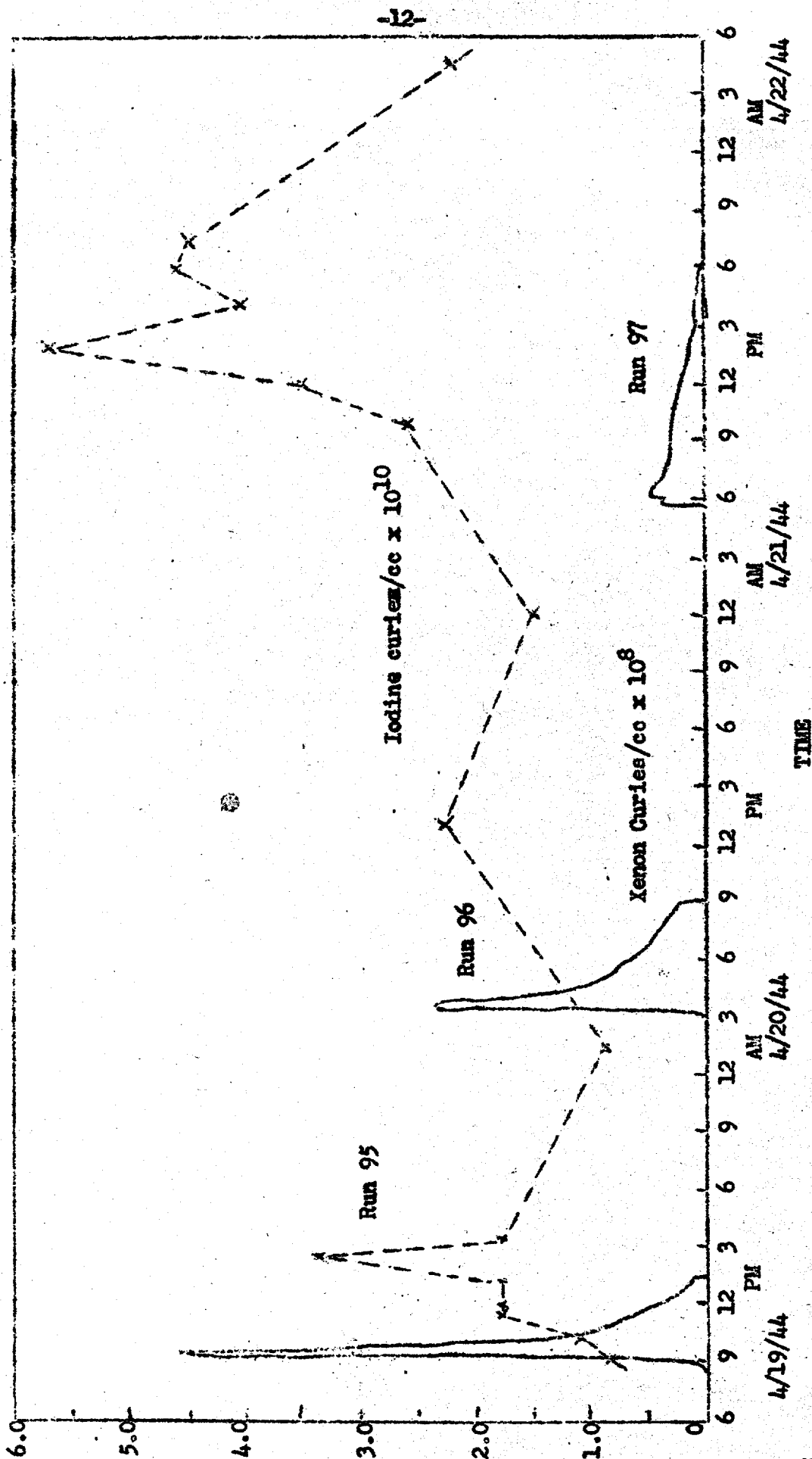
Runs 95, 96, & 97

Figure 4

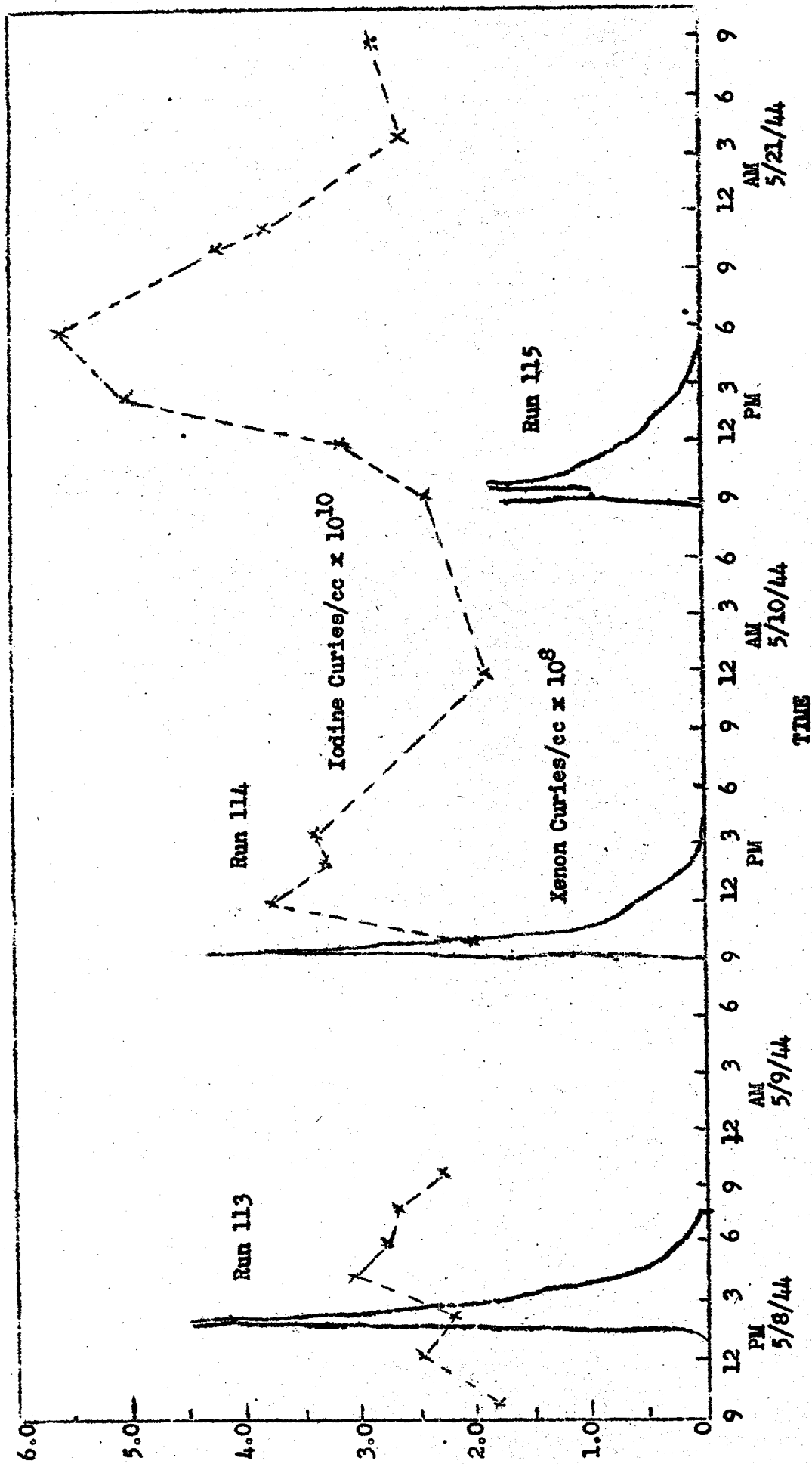DISTRIBUTION OF XENON AND IODINE ACTIVITIES WITH TIME

Runs 113, 114, & 115

Figure 5

In these three runs 8.8, 8.8, and 3.4 millicuries of Xe passed through the monitoring apparatus in a total volume of 3.5×10^6 cc, giving an average Xe concentration in the off-gas of 6.0×10^{-9} curies/cc. During the dissolving the rate of flow in the 4" line rose from about 60 cfm to about 90 cfm, averaging about 80 cfm. Thus, over the 825 minutes of actual dissolving time about 6.6×10^4 cu.ft. or 1.9×10^9 cc of gas was evolved in the 4" line. From these figures one can compute the amount of xenon liberated in the complete cycle to have been 11 curies. This agrees within the experimental error with the amount of xenon, 13.5 curies, calculated to have been in the metal at the time of these 3 dissolvings.

From a period of 3.6×10^3 minutes over the same cycle 1.5 millicuries of iodine were collected from a volume of 8.5×10^6 cc of gas, yielding an average value for the iodine intensity of 1.8×10^{-10} curies/cc. With an average rate of flow in the 4" line of about 85 cu.ft./min., 3.1×10^5 cu.ft. or 8.7×10^9 cc were evolved during this period. The total iodine activity evolved in the dissolver off-gas over the complete cycle is calculated to have been 1.6 curies or 5% of the total expected in the metal at that time.

That not all the iodine is evolved in the solution step is also indicated by the fact that considerable iodine contamination has been detected in cell 2 of the separation plant. In order to determine where the iodine goes samples were taken during Runs 113, 114, and 115, May 8-11, at various stages of the process and are being analyzed. The iodine and xenon activities in the dissolver gas were also closely followed. Figure 5 shows the time distribution of the two activities over the period of the cycle of 3 dissolvings. The iodine curve of the night of May 8 is discontinuous because of a steam failure that stopped the operation of the gas sampling aspirator of the monitoring apparatus for 1-1/4 hrs. during which time the drying traps "froze".

A recording Ring Balance flow meter attached to the orifice in the 4" line made the determination of the off-gas flow much more accurate than during former runs when the flow was estimated from random manometer readings.

The following integrated activities were observed:

	Xenon	Iodine	
Run 113	13.8 curies	.38 curies	(until steam
Run 114	9.8 curies	1.1 curies	failure)
Run 115	7.7 curies	1.5 curies	
	31.3 curies	3.0 curies	

The expected activity of xenon and iodine in the metal dissolved is computed from the following factors:

Total xenon activity in pile at 1000 kw	4.35×10^4 curies
Total iodine activity in pile at 1000 kw	1.92×10^4 curies
Fraction pile metal in charge	.03
Average hold-up time	31 days
Fraction Xe activity after hold-up decay	.017
Fraction iodine activity after hold-up decay	.069
Average intensity factor	1.54

Xenon activity = $4.35 \times 10^4 \times .03 \times .017 \times 1.54 = 34$ curies
Iodine activity = $1.92 \times 10^4 \times .03 \times .069 \times 1.54 = 68$ curies

Of the calculated 34 curies of xenon 31.3 curies, or 100% within the experimental error, were observed to pass from the dissolver to the stack and 3 curies of iodine, or about 4.4% of the calculated 68 curies were observed to pass from the dissolver to the stack.

V. Stack Drainage Analysis

During Runs 47 and 48 (reported in M-CP-1400) samples of the stack drainage were collected by Mr. Vincent of the Plant Assistance group and given us for analysis. The concentration of iodine in these samples indicated that during Run 47 about 10 millicuries were dissolved in the drain water over an eight hour period and during Run 48 about 6 millicuries were dissolved over a 4 hour period. Assuming an off-gas flow rate of 100 cfm, the corresponding volume for Run 47 was about 4.8×10^4 cu.ft. and for Run 48 3.6×10^4 cu.ft. For Run 47 the average iodine concentration was 4×10^{-6} curies/cu.ft. so that the amount of iodine in the dissolver gas was $4 \times 10^{-6} \times 4.8 \times 10^4$ curies or 200 millicuries. These figures indicate 5% of the iodine activity in the off-gas was absorbed in the stack drainings.

During Run 48 the average iodine concentration for this period was 7×10^{-6} curies/cu.ft. The total iodine activity up the stack, then, during the 8 hour period was about $3.6 \times 10^4 \times 7 \times 10^{-6}$ curies or 250 millicuries. The fraction absorbed in the drainings was about 2-1/2%.

At the time these measurements were made there were no instruments for recording the off-gas flow rate and these figures give only a general idea of fraction of off-gas iodine activity dissolved in the stack drainings.

VI. Tabulation of Data over Two Month Period

Table II gives a tabulation of the observations made on scattered runs over a two month period. At this time the monitoring apparatus was

not in continuous operation and the arrangement of the apparatus, the scrubbing solutions, and the drying apparatus was changed from time to time. The time intervals over which the iodine was collected in the traps does not necessarily coincide with the time of the dissolving and many intervals are so long that the efficiency of the scrubbers may have dropped by a factor of 2 or more.

VII. Suggestions for Continuous Monitoring

Satisfactory continuous records of the xenon activity have been obtained since the iodine contamination of the stainless steel chamber was overcome. The measurements of the active iodine concentrations have been made by daily checks of the scrubbing water. This process is time consuming and inaccurate since it is known that the traps lose their efficiency unless changed regularly.

Even though it is likely that some of the ion chamber contamination collected with the water in the chamber, it still seems advisable to remove both the iodine and the water from the gas. The iodine measurement can then best be done after it has been removed from the xenon.

A trial chamber (Figure 6) in which water containing the iodine passes through 1/8" O.D. saran tubing wound in a tight helix on the inside of the high voltage electrode has been constructed. This tubing has a wall thickness of 0.015" and its availability was suggested by W. Q. Smith. About 190 feet of the tubing are in the chamber and hold 250 cc of water. An ion current of 10^{-12} amp was obtained for 3×10^{-6} curies of iodine in the chamber. Saran tubing of 1/4" O.D. was also tried, but the sensitivity of the chamber is reduced by a factor of about 20.

Since the iodine concentration in the off gas is about 1×10^{-10} curies per cc, the iodine from about two cubic feet of the gas will have to be in a chamber of the type shown in Figure 6 in order to get one half scale deflection on a Beckman amplifier having .4 volts full scale sensitivity.

A continuously monitoring system can be designed involving a continuous flow of both gas and water. This involves a rather careful adjustment of pressure differentials. In order to achieve a minimum delay in recording a change in iodine concentration the volume of the water in the scrubber and in the chamber should be equal. In order to meet the conditions stated in the previous paragraph a gas flow of 0.2 cfm and a water flow of 25 cc per minute or a gas flow of 0.1 cfm and a water flow of 12.5 cc per minute could be used. In the first example there would be a 10 minute delay time, in the second 20 minutes.
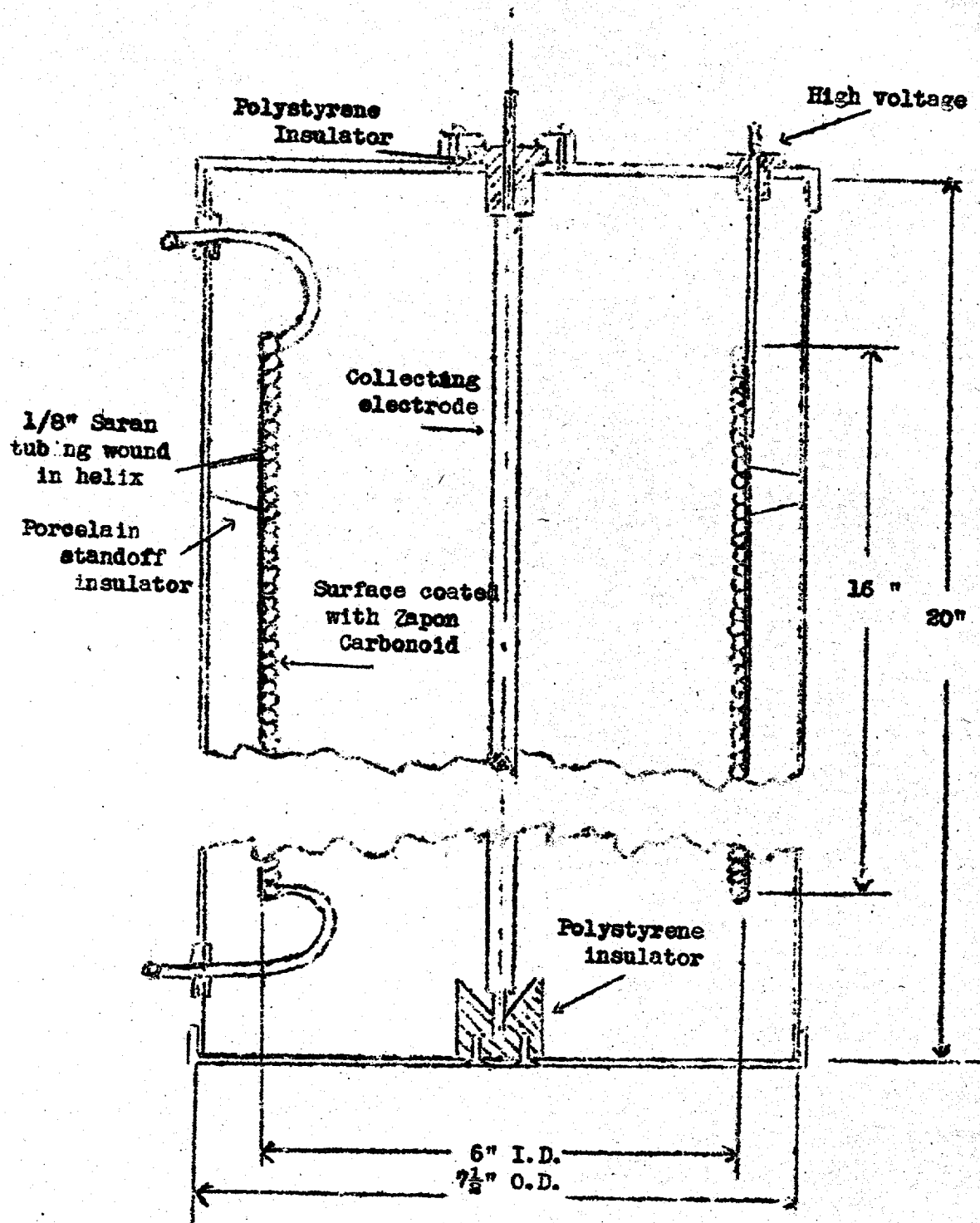
Table II

TABULATION OF OBSERVATIONS OF XENON AND IODINE INTENSITIES IN THE DISSOLVER OFF-GAS ONE TWO-MONTH PERIOD

Date	Run	Xenon Peak Activity Time	Xenon Peak Activity Curies/cc x 10^9	Xenon Average Activity Time Int. (hrs.)	Xenon Average Activity Curies/cc x 10^9	Iodine Activity Time Int. (hrs.)	Iodine Activity Curies/cc x 10^11
3/19/44	68	9:30 PM	5.6	8	1.5	30	14
3/23/44	72	10:35 AM	60	4	20	19	18
3/24/44	73	1:30 AM	11	18	2.7	24-1/2	6.2
3/30/44	80	4:00 PM	4.8	18	.80	20-1/2	6.0
3/31/44	81	7:00 PM	14	3-3/4	5.6	} 47	7.3
4/1/44	82	12:50 PM	22	4-1/2	5.0	}	
4/2/44	83	1:00 PM	10	10	1.7	15-1/4	5.8
4/5/44	84	8:30 PM	5.6	13-1/2	1.5	7	7.1
4/6/44						23	5.2
4/7/44						7	6.7
"	85	3:30 AM	4.0	8	1.6	10	5.3
4/8/44	86					5-1/4	7.7
"						42	19
4/10/44	87					6	9.5
4/11/44	88					21	5.2
4/12/44						17	8.3
4/13/44	89	3:00 PM	6.8	7	2.1	18-1/2	3.3
"	95	9:30 AM	48	4-1/6	12	6	18
4/20/44	96	3:30 AM	24	6-1/4	7.6	19	15
4/21/44	97	6:00 AM	5.6	11-2/3	2.2	24	30

Figure 6

Sketch of Saran Helix Chamber

Polystyrene Insulator

High voltage

1/8" Saran tubing wound in helix

Porcelain standoff insulator

Collecting electrode

Surface coated with Zapon Carbonoid

Polystyrene insulator

16 "

20"

6" I.D.
7½" O.D.

The actual saran tube chamber described above is not recommended because a 6 ft. head of water caused a flow of only 6.5 cc of water per minute through it. The use of 4 tubes in parallel with the same total length of tubing in the chamber should give 25 cc per minute with a 1-1/2 foot water head. Pumps which produce pressure surges should not be used to induce the water flow since it has been found that the amplifier is very unstable under such conditions.

Footnote for page 8

* After this report had been prepared for publication the results from the iodine analysis of two standardizing solutions were received from Mr. R. I. Martens of the Analytical Division. These figures indicate a calibration of 9.1×10^{-8} curies/cc/div/min. This is about 1.6 times the value used in the calculations of iodine intensities in this and previous reports.

The methods used in this analysis involved the reduction of iodate, found in the scrubbing solution, to iodide before the iodide separation by a procedure similar to the one outlined in this report. It is believed that more of the iodine activity in the scrubbing solution is precipitated out than formerly and hence this calibration is more nearly correct.